Advanced Heat Transfer and Thermal Storage Fluids

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Goals and Objectives

- The goal is to find a heat transfer and thermal storage fluid with a usable liquid range from near 0 to above 400 °C that will meet the cost and performance requirements of parabolic trough systems.

- The near term objective (FY03) is to identify a fluid with the potential for service up to 300 °C.

Project to Date

- Synthesis and thermal stability of imidazolium salts and identification of other possible salts – NREL FY2000-present

- Physical properties, materials compatibility, and extended thermal stability testing – The University of Alabama FY2001-present

- Production Process and Cost Study - Peak Design Subcontract FY02

The Challenge for A New Fluid

- Low freezing point - <25 °C
- Low vapor pressure - < 1 atm at T_{max}
- Low cost - < ~$4.50/Kg
- Thermal stability at > 400 °C
- Compatible with alloys and materials used in solar plants
- Other physical properties compatible with the solar application

Imidazolium Salts

R_4 R_3

R_5 R_2

R_1

R_4 R_3
R_5 R_2
R_1

$X^{\ominus}$

$X^{\ominus}$
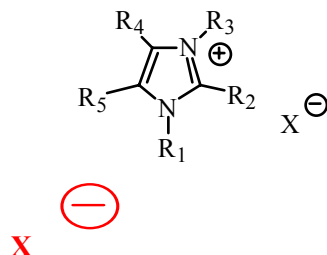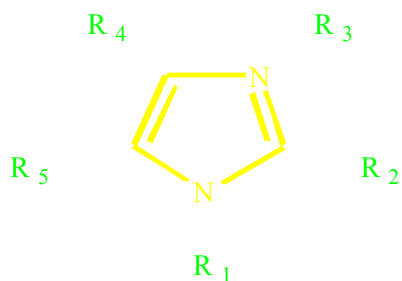
R

Methyl
Ethyl
Butyl
Hexyl
Octyl
Phenyl
Silyl

X$^{\ominus}$

Cl$^{\ominus}$

$^{\ominus}$**OSO$_2$CH$_3$**

BF$_4$ $^{\ominus}$

PF$_6$ $^{\ominus}$

Table 1. Cost of reactants for synthesis of EmimBF$_4$

Reactant	Cost ($/lb)	Cost per lb of EmimBF$_4$
Glyoxal (50%) (ethylene glycol)	1.00 (0.38)	**.73 (0.12)**
Formaldehyde	.21	**.03**
Ammonia	.10	**.01**
Methylamine	.73	**.11**
Ethylchloride (ethylene)	2.00 (0.23)	**.64 (0.03)**
Tetrafluoroboric acid (50%)	**.65**	**.58**

Process Changes to reduce the cost of an imidazolium salt
Peak Design (2002)
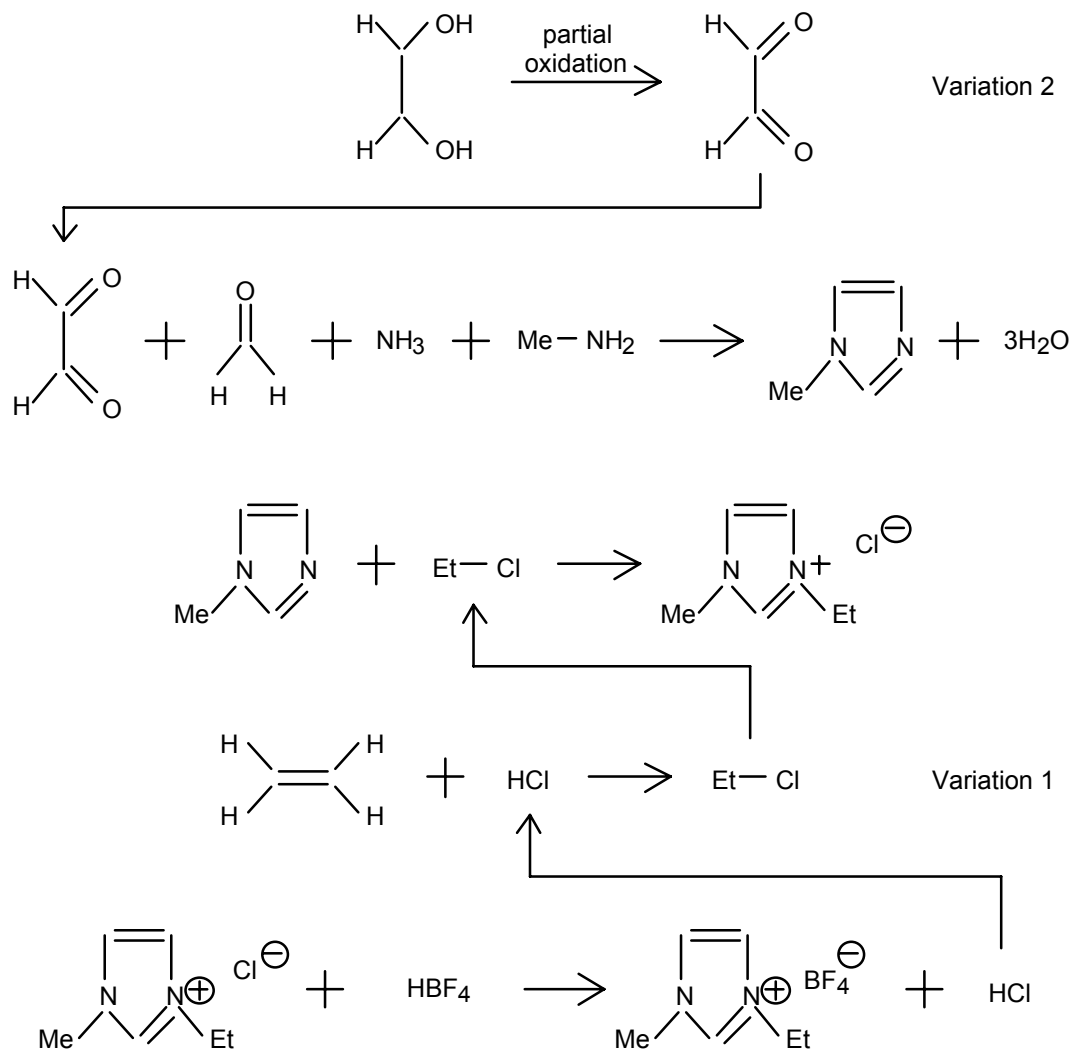
Production process for ethylmethylimidazolium Tetrafluoroborate (process 3)
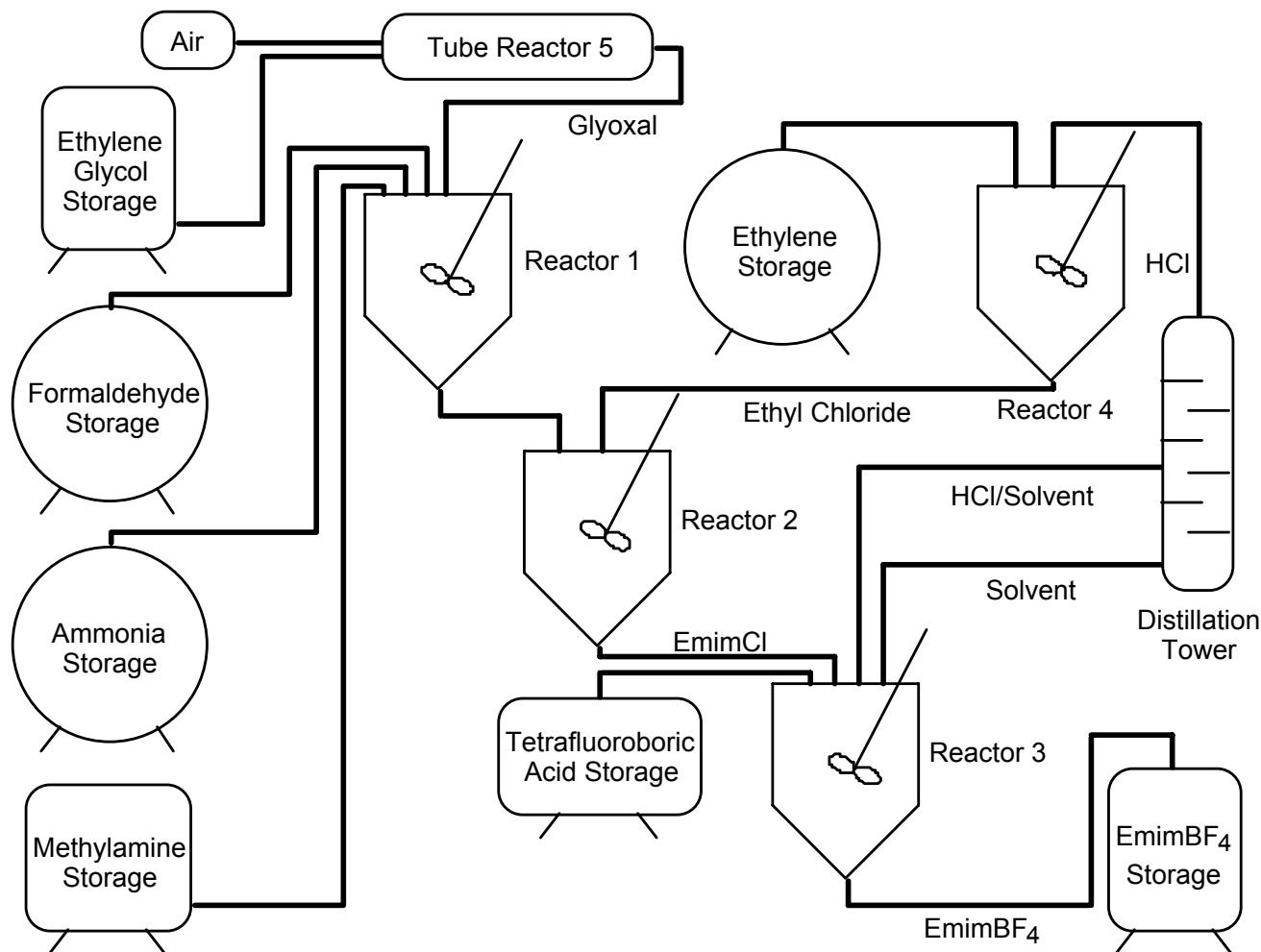
Table 3. Economic assumptions for the discount cash flow analysis
Peak Designs (2002)

Economic Factor	Value
Internal Rate of Return	15%
Depreciation	**Tab. 4**
Recovery Period	11 years
Plant Life	21 years
Construction Period	1 year
Working Capital	15% of total capital
Federal Tax	40% of net income
State Tax	5% of net income
Salvage Value	10% of fixed capital
Debt/Equity Ratio	0/100
Plant size	10,000,000 kg/yr
Annual hours of operation	8,322 (95%)
Labor	$50/hr (loaded including supervision)
Maintenance	7% of fixed capital
Electricity	$0.06/kWhr
Reaction yields	100% (except glyoxal synthesis: 75%)

Table 7. Required costs for $EmimBF_4$

Process	Reactant costs	Other operating	Capital	TotalCost ($/kg)
1	4.75	0.24	0.37	5.36
2	3.30	0.25	0.37	3.92
3	**2.02**	**0.25**	**0.39**	**2.66**

Table 8. Product cost dependence on plant size and internal rate of return

Process	Plant Size (10^6 kg/yr)	Product Cost ($/kg)
1	5	5.57
	10	5.36
	50	5.16
2	5	4.16
	10	3.92
	50	3.70
3	**5**	**2.90**
	10	**2.66**
	50	**2.43**

Process	IRR (%)	Product Cost ($/kg)
1	10	5.24
	15	5.36
	25	5.62
2	10	3.80
	15	3.92
	25	4.19
3	**10**	**2.53**
	15	**2.66**
	25	**2.92**

Table 9. Cost of EmimBF$_4$ as a function of reaction yield (process 3)

Reaction Yields*	Total cost ($/kg)
100%	$2.66
95	2.86
90	3.11
80	3.85

*Glyoxal yield is held at 75% in all cases

Summary and Conclusions

- Cost goals can be met with an organic salt
- When a viable candidate is identified the production process must be optimized

Longer term stability test of [C$_8$mim]PF$_6$

U of Alabama, 2001
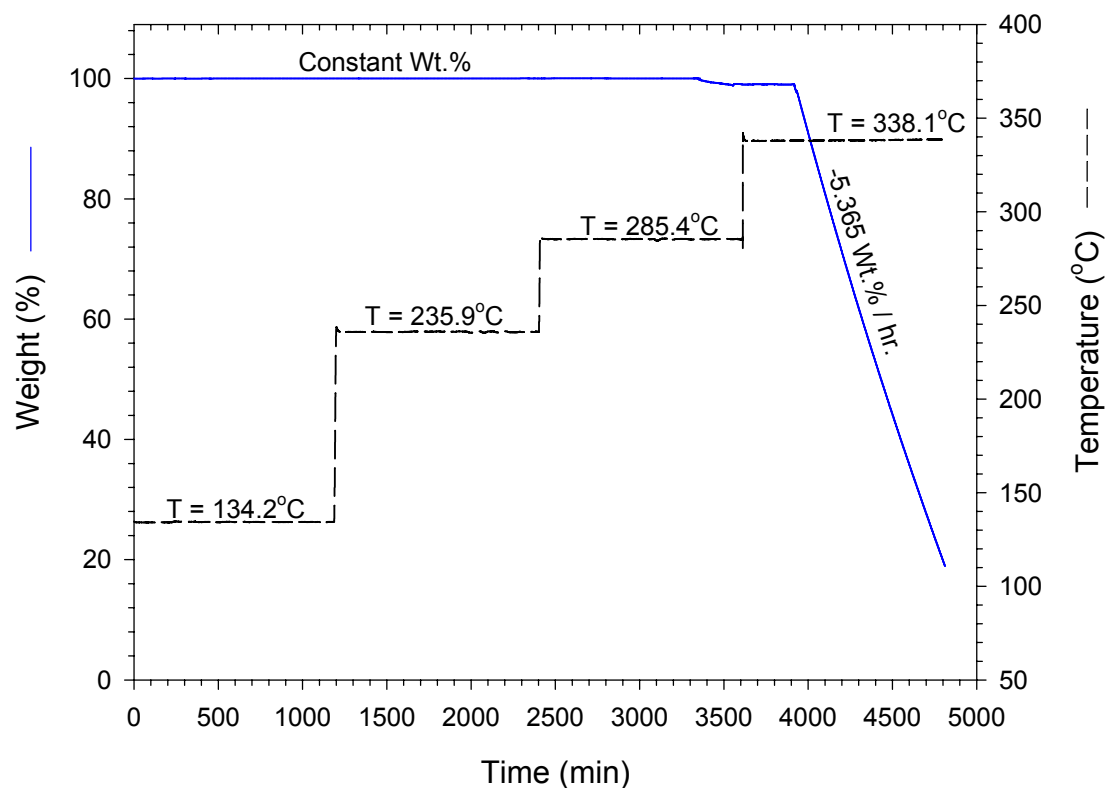
Overall Observations

- We may have pushed the upper temperature limit of imidazolium salts as high as possible with anions – Further improvements may require changes in the imidazolium ring substituents

- A 300 °C salt appears to be within reach

- We will begin some work on alternative types of organic salts and mixtures
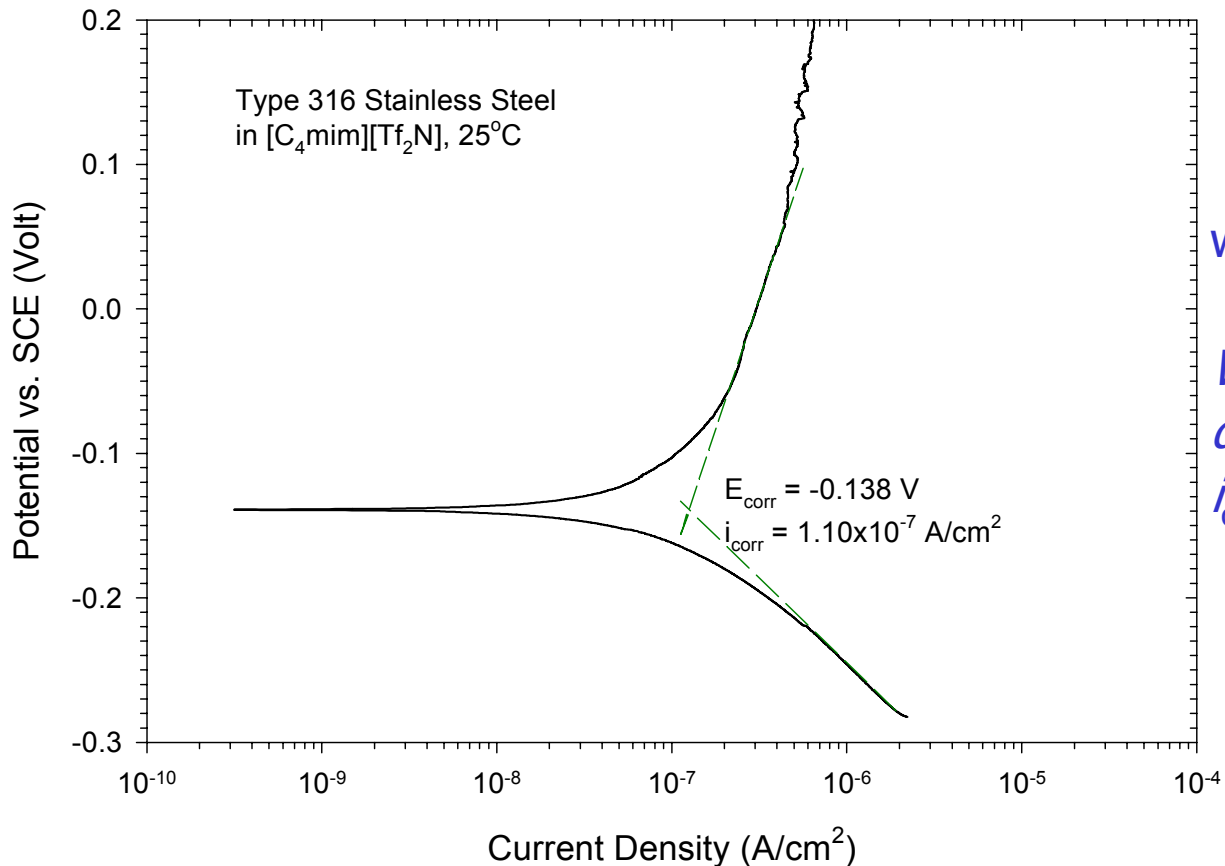
Corrosivity of Ionic Liquids

Experimental Methods

◆ Tafel extrapolation method was used to determine corrosion current density and calculate corrosion rates

◆ Potentiodynamic polarization curves to analyze corrosion behavior of the alloys in ionic liquids

◆ Experiments were performed at room temperature

◆ Alloys tested:

  - 1018 carbon steel

  - 316 stainless steel

  - gray cast iron

Typical Tafel Plot

Type 316 Stainless Steel
in [C$_4$mim][Tf$_2$N], 25°C

E_{corr} = -0.138 V

i_{corr} = 1.10x10^{-7} A/cm^2

Potential vs. SCE (Volt)

Current Density (A/cm^2)

$$r = \frac{3.27 \times 10^{-3} \cdot i_{corr} \cdot W}{d}$$

where:

r = corrosion rate (mm/yr)

W = equivalent weight (g)

d = alloy density (g/cm^3)

i_{corr} = corrosion current
density (μA/cm^2)

Uniform Corrosion Rates of Solar Materials in Ionic Liquids

Ionic liquid	Corrosion Rate at 25°C, in μm/yr		
	SS 316	1018 Carbon Steel	Gray Cast Iron
$[C_4mim]Cl$	1.3 LC	3.2 LC	8.9 LC
$[C_8mim]PF_6$	1.2	5.6	2.6
$[C_6mim]PF_6$	0.4	13.0	13.0
$[C_4mim][Tf_2N]$	1.1	11.0	20.0

LC = localized corrosion

Conclusions

◆ Materials used in solar plant technology such as 316 stainless steel alloy, 1018 carbon steel and gray cast iron were found to be outstanding in corrosion resistance (corrosion rates: <20 μm/yr) against ionic liquids at RT

◆ Localized corrosion was observed on the surface of the materials exposed to [C$_4$mim]Cl ionic liquid

◆ The potentiodynamic tests showed in most cases an active/passive corrosion behavior. However, the ionic liquid [C$_4$mim]Cl prevented the formation of stable passive films

Heat Capacities

Properties of Heat Transfer Fluids at 25°C

Liquid	Melting point, °C	Density g/ml	Viscosity cPs	Cp Jg^{-1}K^{-1}	Cp, v Jcm^{-3}K^{-1}
Dowtherm HT	NA	1.01	953	1.42	1.41
Thermal oil	NA	0.89	1.9	1.69	1.90
[C$_4$mim]Cl	57.1	1	NA	1.58	>1.58
[C$_2$mim][BF$_4$]	5.8	1.20	34	1.12	1.34
[C$_2$mim][PF$_6$]	60.5	1.10	NA	1.00	1.10
[C$_4$mim][PF$_6$]	6.5	1.37	389	1.14	1.56
[C$_6$mim][PF$_6$]	-80(T$_g$)	1.30	688	1.34	1.75
[C$_4$mim][Tf$_2$N]	-5.1	1.44	53	1.05	1.50

A comparison of Volumetric Heat Capacity Performance
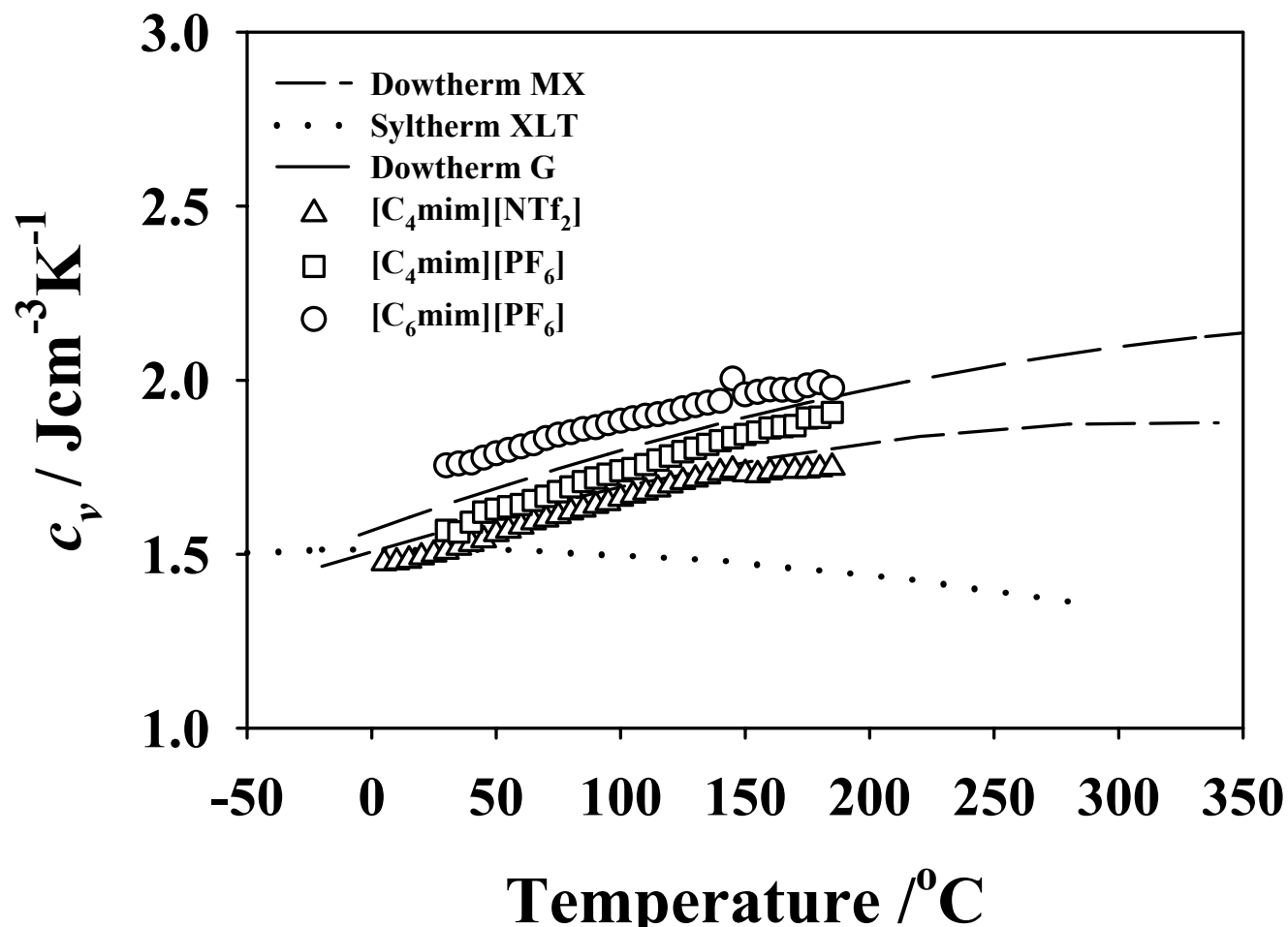
Viscosities of Ionic Liquids

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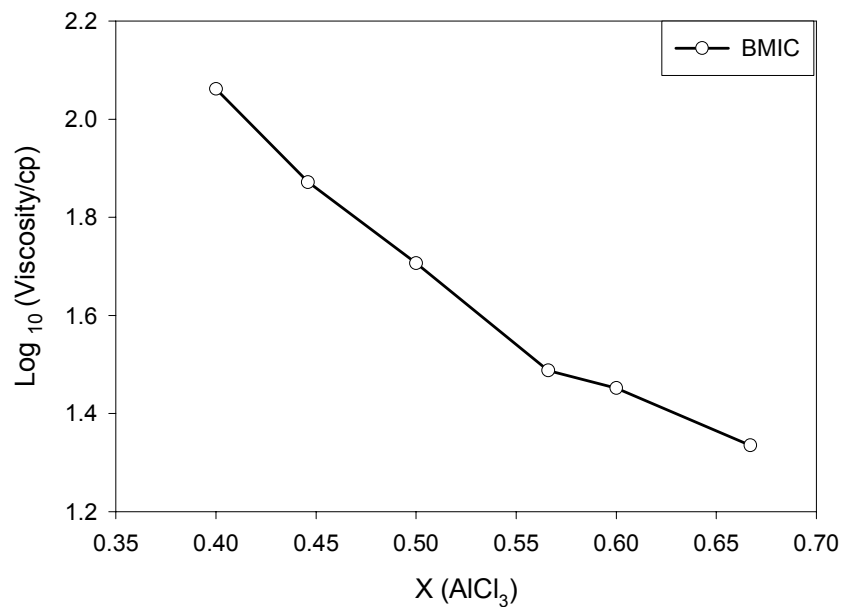
C_4mimCl at 300K
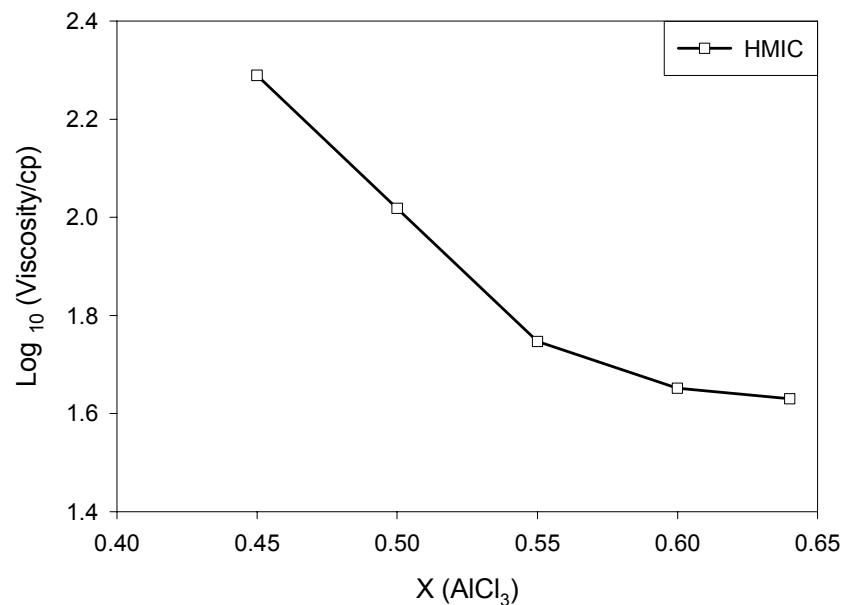
C_6mimCl at 300K

Long Term Thermal Stability of IL

Evaluation of Long-term Thermal Stability

◆ Experimental Procedure :

- Hold the ionic liquid samples at a fixed temperature for 20 hours,

- Then raise the temperature to a higher level and holding for another 20 hours until significant weight changes are observed.
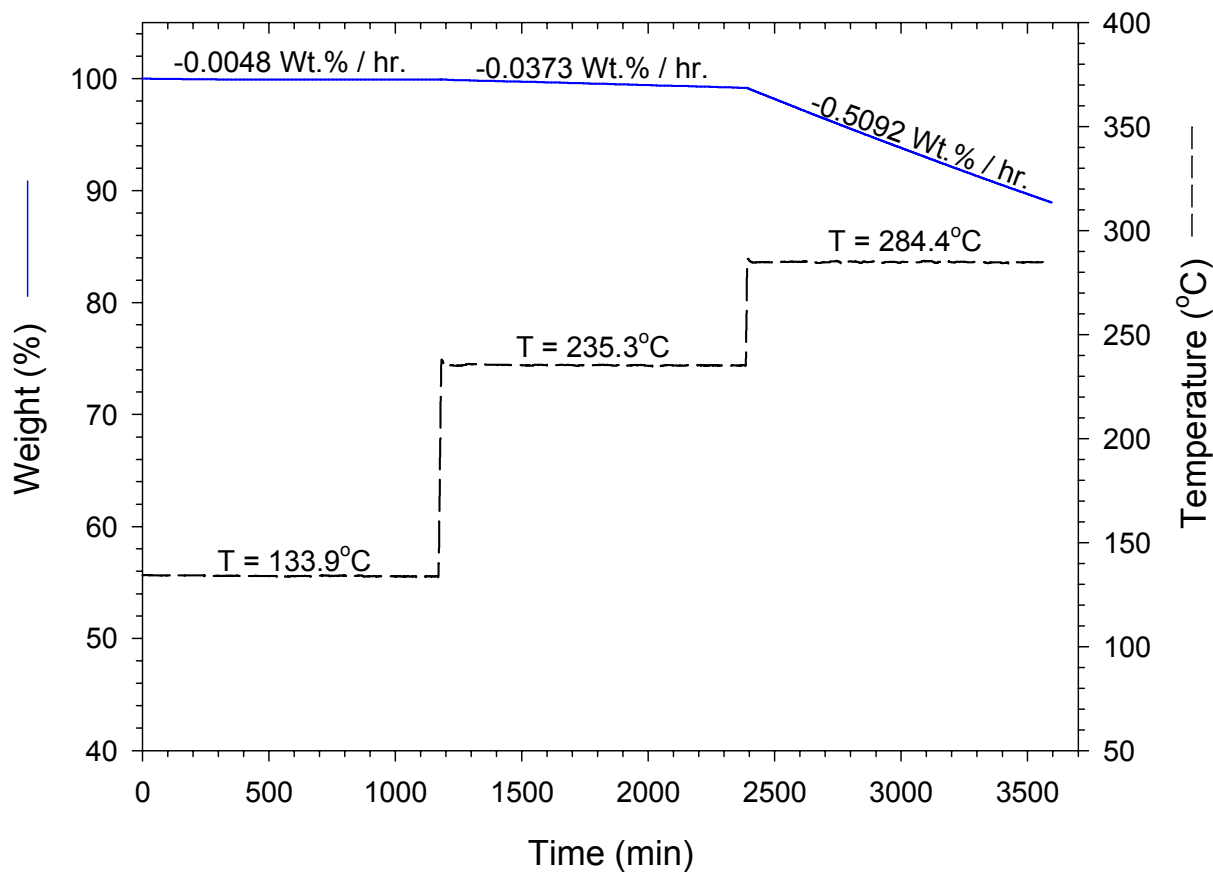
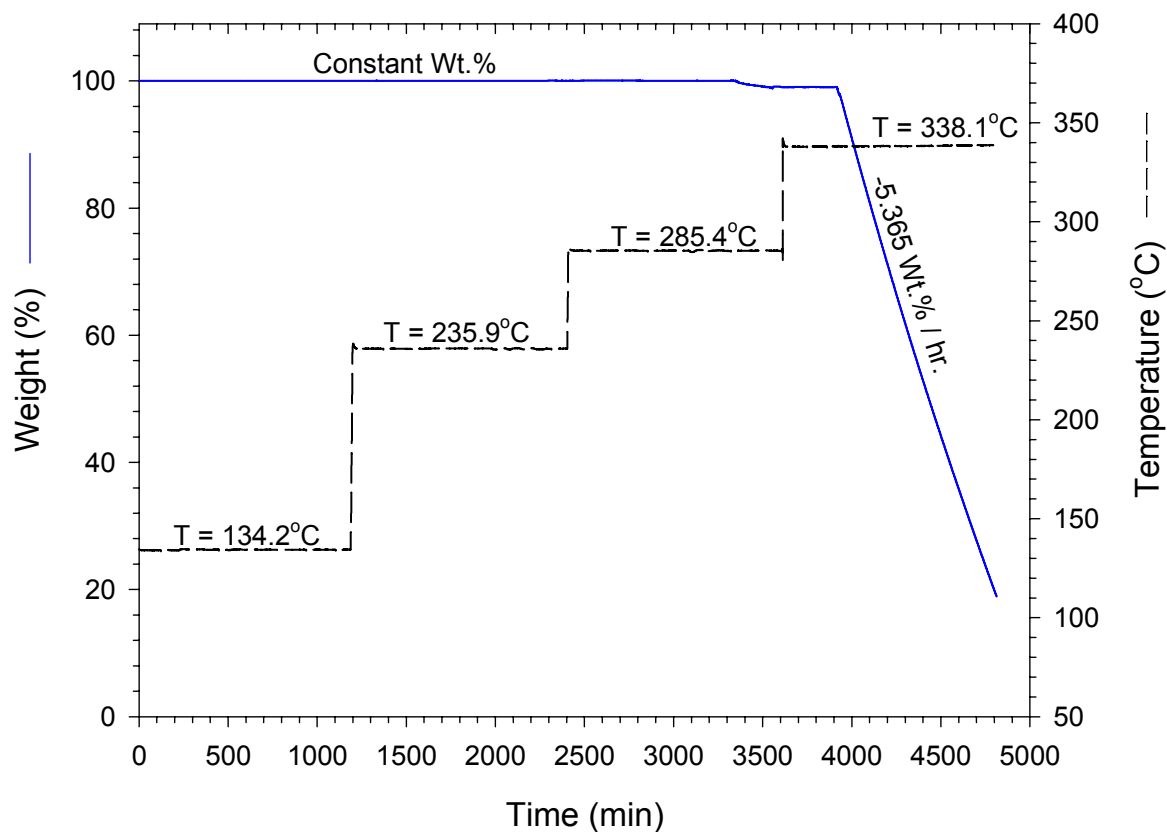# *Weight Changes of [C₄mim][Tf₂N] as a Function of Time at Different Temperatures*
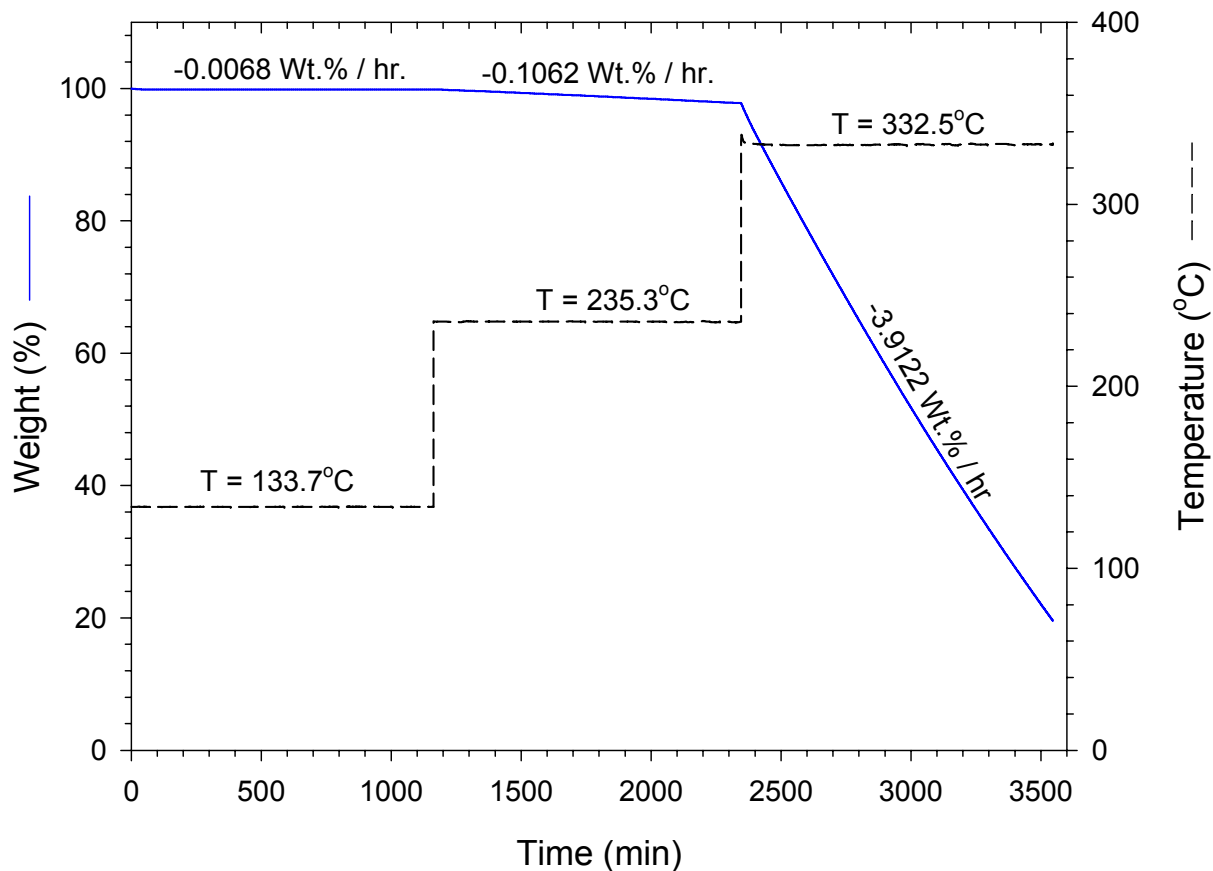
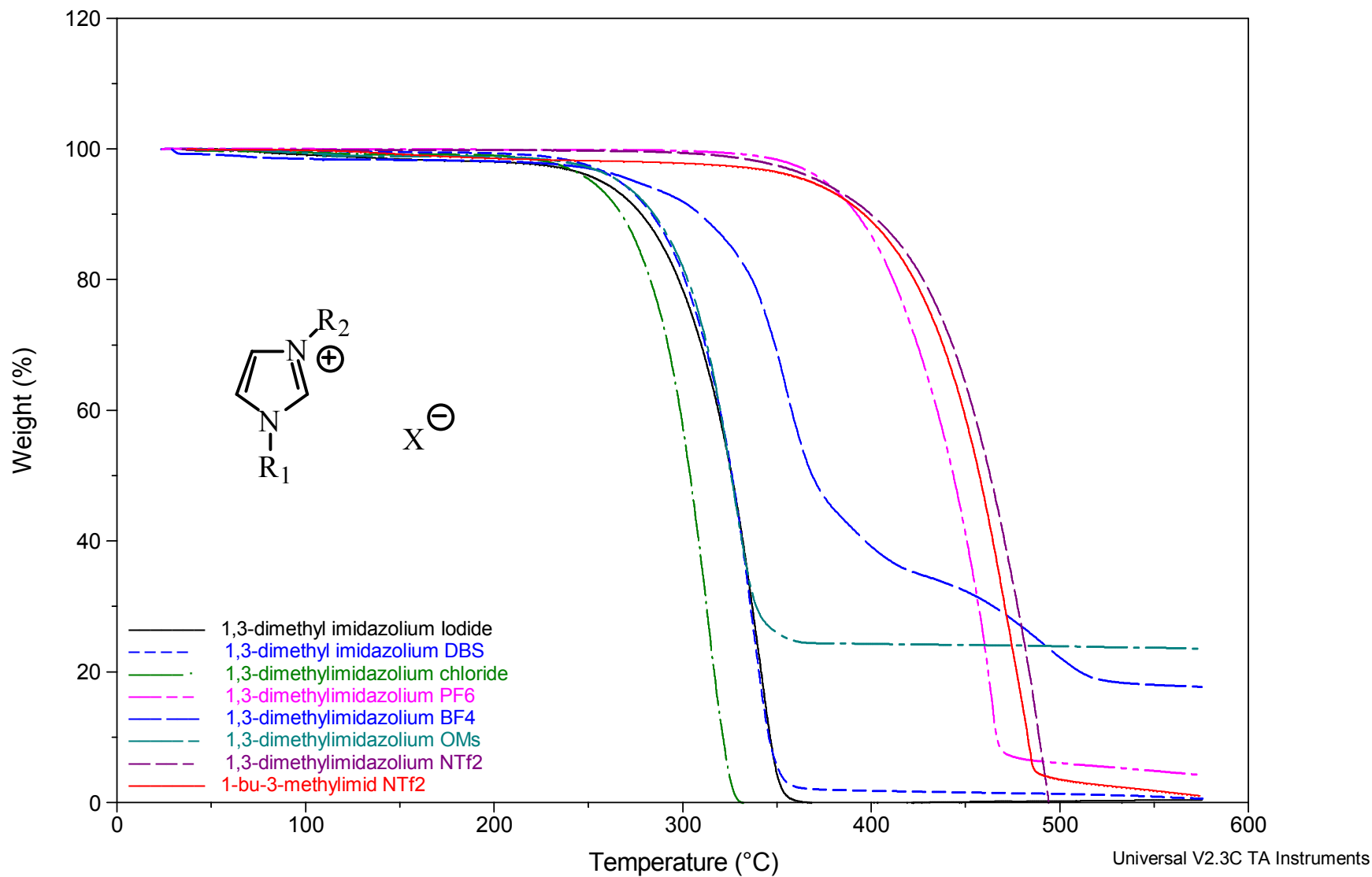# *Weight Changes of [C$_6$mim]PF$_6$ as a Function of Time at Different Temperatures*

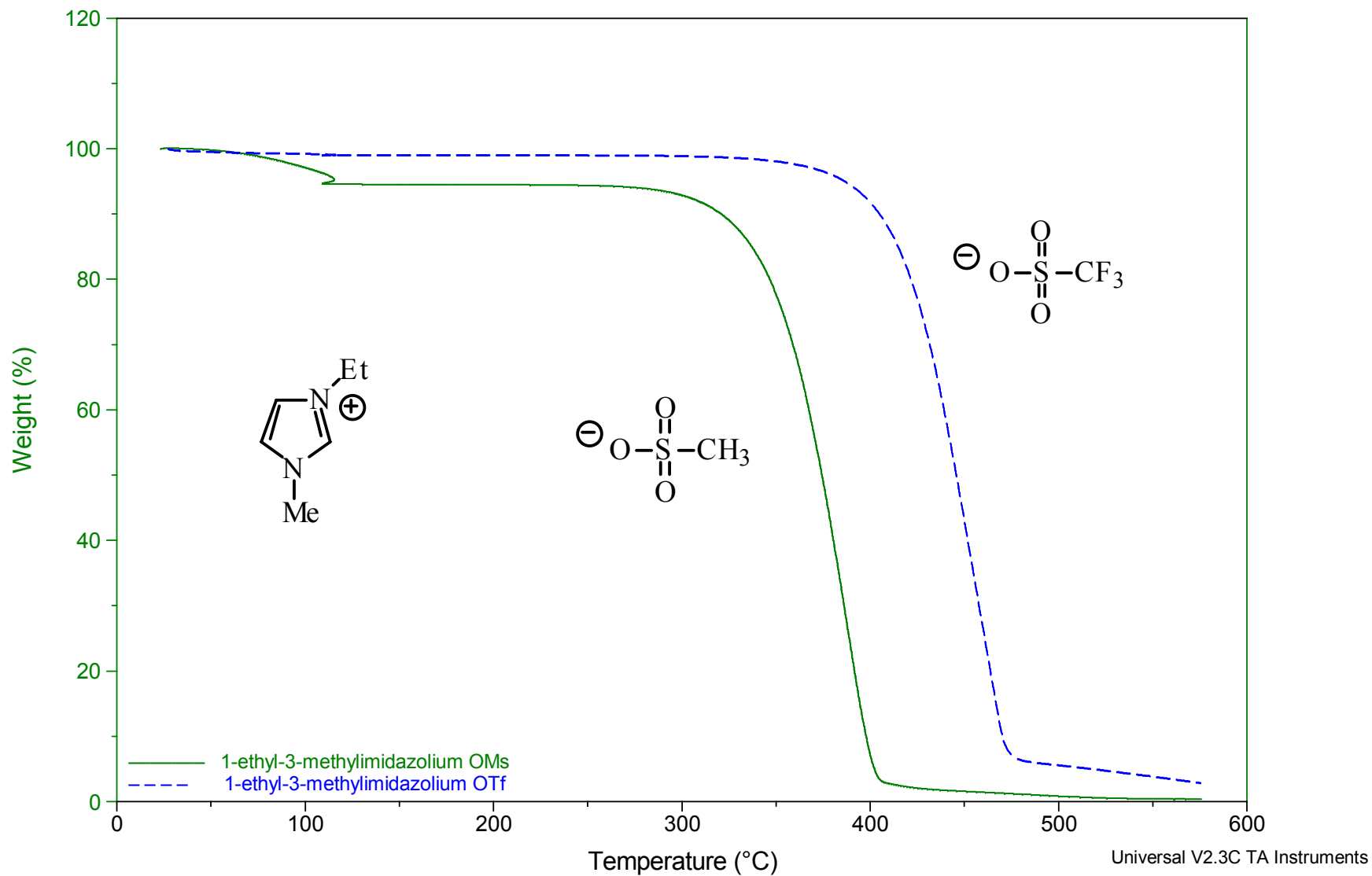# Weight Changes of [C$_8$mim]PF$_6$ as a Function of Time at Different Temperatures

Influence of ANION

Legend:
- 1,3-dimethyl imidazolium Iodide
- 1,3-dimethyl imidazolium DBS
- 1,3-dimethylimidazolium chloride
- 1,3-dimethylimidazolium PF6
- 1,3-dimethylimidazolium BF4
- 1,3-dimethylimidazolium OMs
- 1,3-dimethylimidazolium NTf2
- 1-bu-3-methylimid NTf2

Axis labels: Weight (%) vs Temperature (°C)

Universal V2.3C TA Instruments

Influence of ANION

Legend:
- 1-ethyl-3-methylimidazolium OMs
- 1-ethyl-3-methylimidazolium OTf

Universal V2.3C TA Instruments

Influence of CATION structure

Weight (%) vs Temperature (°C)

- 1,2,3,4,5-pentamethylimid PF6
- 1,3-dimethylimidazolium PF6
- 1,3,4,5-tetramethylimid PF6

Universal V2.3C TA Instruments
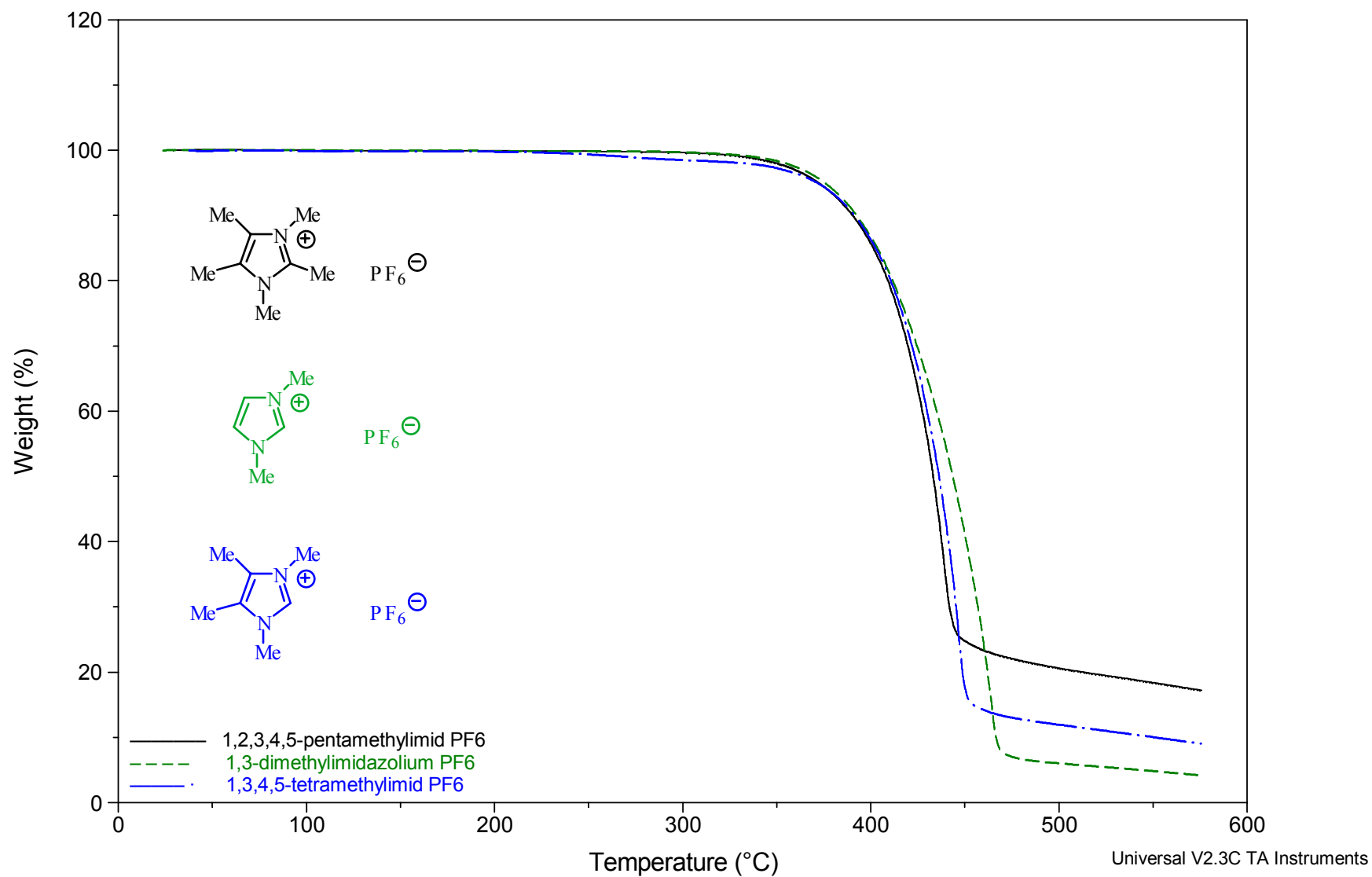
Ramp 20C/min and Isothermal decomposition over 120 min

Weight (%)

Temperature (¡C)

199.97¡C
99.08%

299.63¡C
58.67%

375.46¡C
0.9011%

Bu

N⊕

⊖N

SO₂CF₃

SO₂CF₃

Me
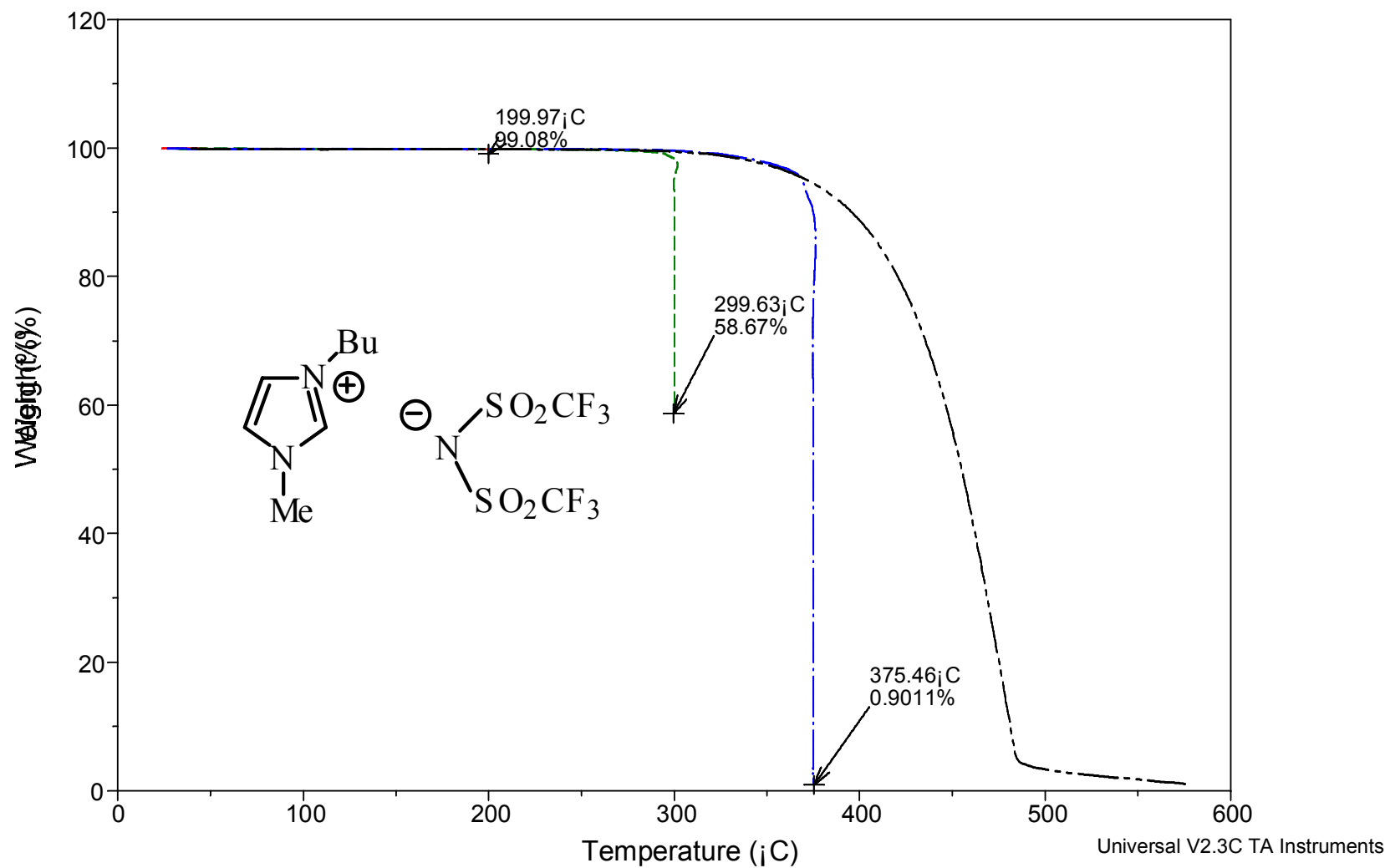
Schematic of NREL's MBMS Sampling System

Products and Transients

Three Stage Free-Jet Molecular Beam Source

Triple Quadrupole Mass Analyzer

Reactants

Reactor with heat or photons or catalyst

e⁻

EI Source

Q1 **Q2** **Q3**

Collisions

{P⁺}   →   {D⁺}

Detector

Molecular Drag Pump

Turbomolecular Pump

Turbomolecular Pump

Argon Collision Gas

Turbomolecular Pump
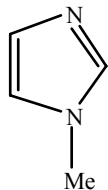
NREL
National Renewable Energy Laboratory
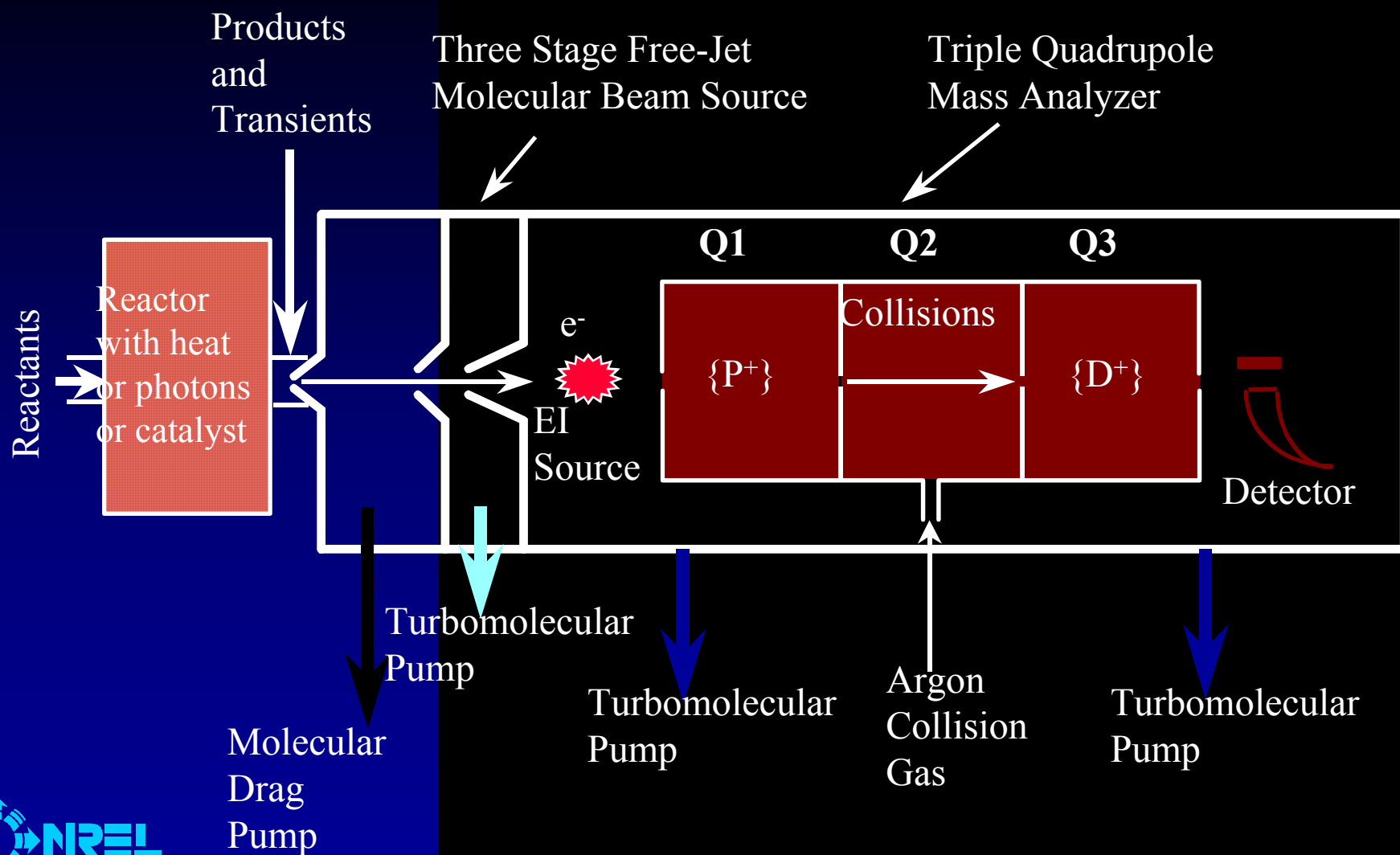
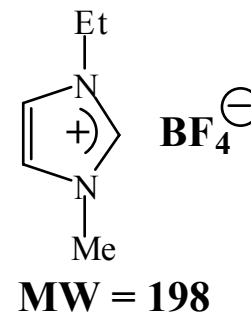# Thermal Decomposition Pathways

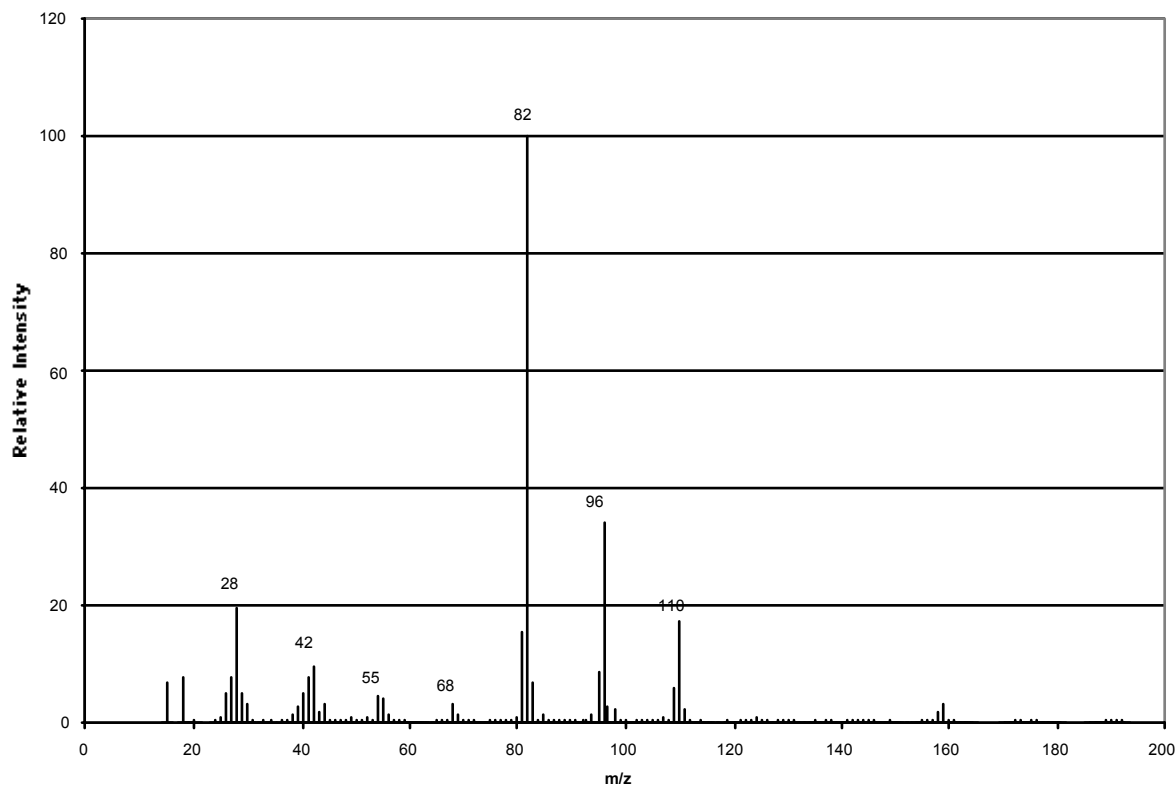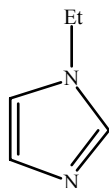## Demethylation
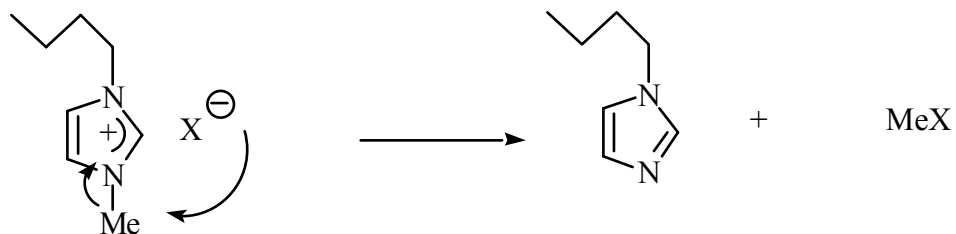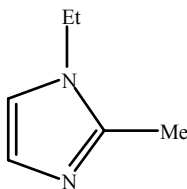

Hofmann Type Elimination
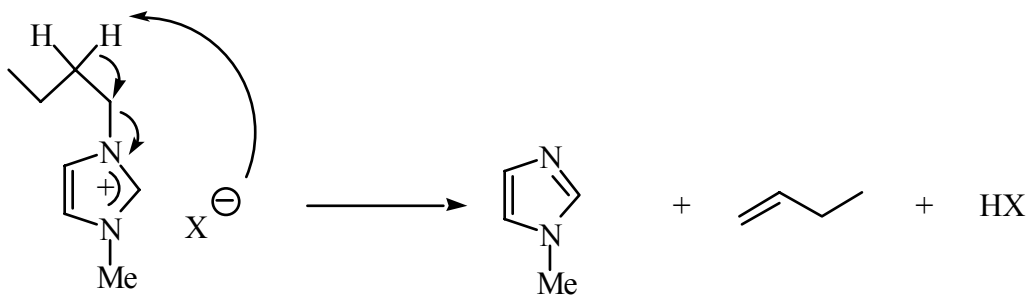
MBMS study of [EtMeIm][BF$_4$]

MW = 198

m/z = 82

m/z = 96

m/z = 110

Proposed thermal events :

1) HF liberation at high T
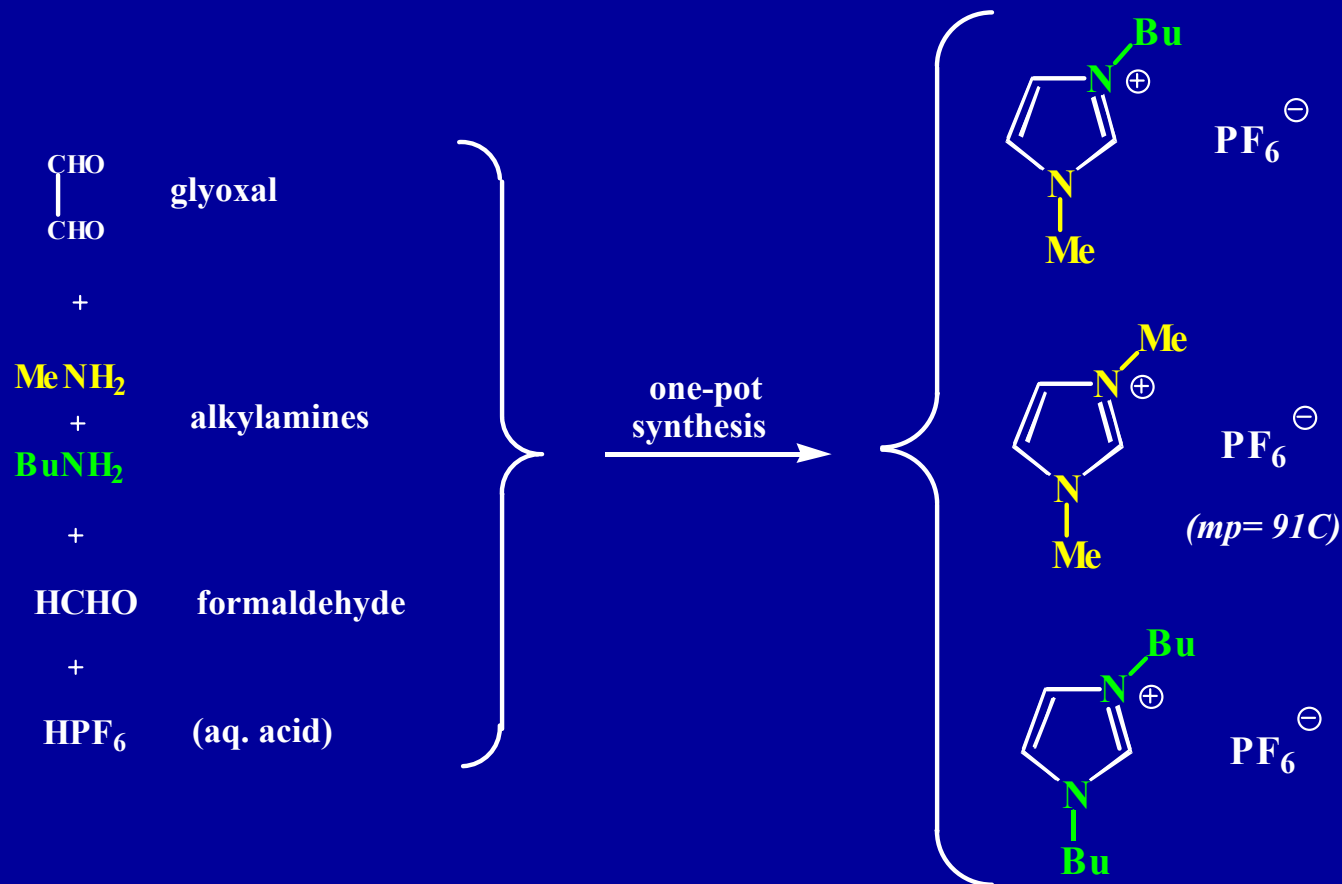
2) de-alkylation of quat. amine salt

One-Step Synthesis of Ionic Liquids

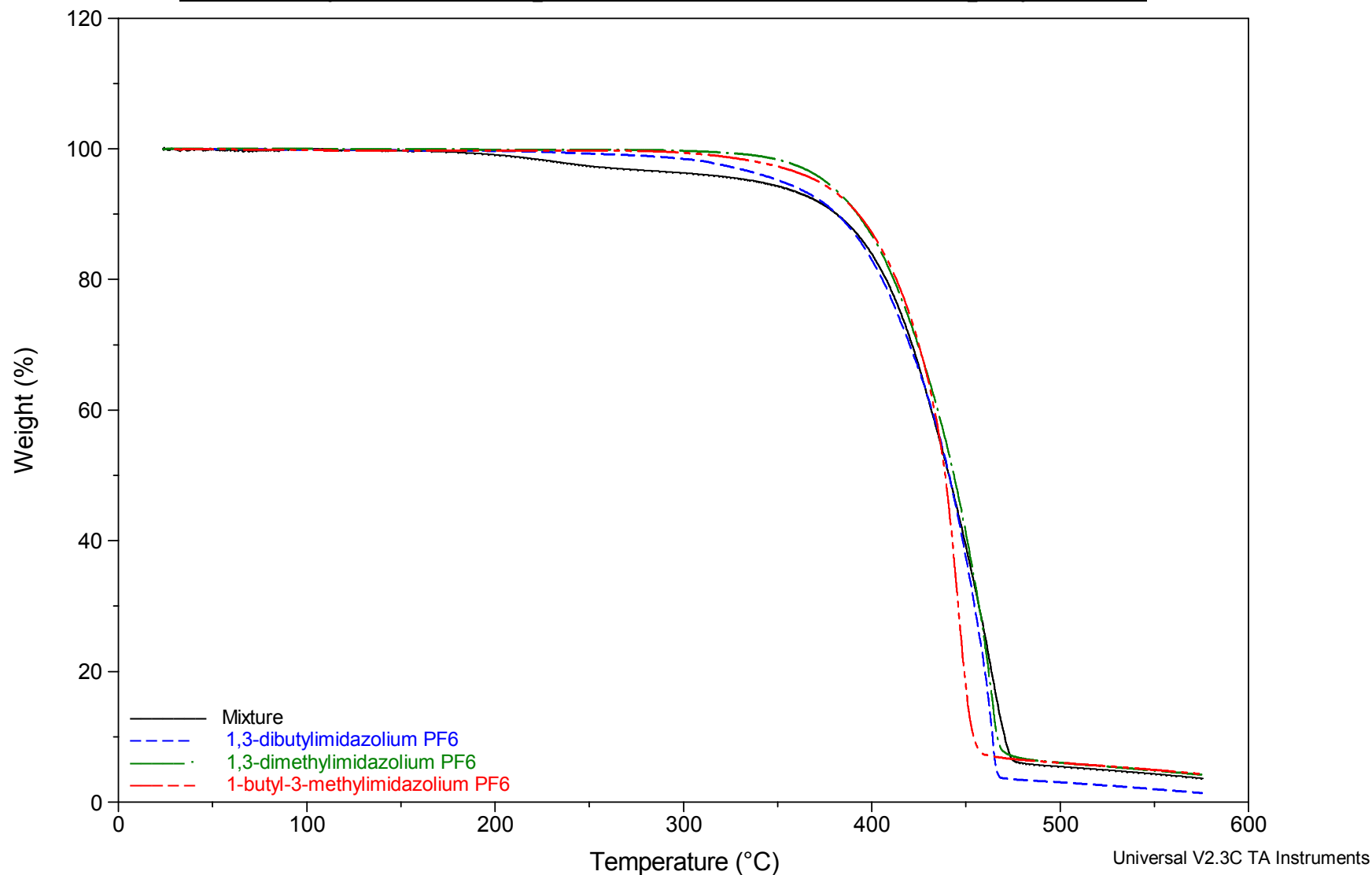| CHO | glyoxal |
CHO	
+	
MeNH₂	alkylamines
+	
BuNH₂	
+	
HCHO	formaldehyde
+	
HPF₆	(aq. acid)

one-pot synthesis →

(mp= 91C)

* avoids chloride salts as intermediates !

* 'adjustment' of melting point and thermal stability

T stability of Ionic Liquid Mixture from One-Step Synthesis

Weight (%) vs Temperature (°C)

Legend:
- Mixture
- 1,3-dibutylimidazolium PF6
- 1,3-dimethylimidazolium PF6
- 1-butyl-3-methylimidazolium PF6

Universal V2.3C TA Instruments

Conclusions

- **Imidazolium salts offer flexibility in 'designing' melting point and thermal stability**

- **PF_6 salts are 'easy' to prepare and purify, and are probably least expensive**

- **Onset T for thermal decomposition must be determined carefully. Kinetic data are needed for evaluation of long-term T stability**

- **Reactivity of ANION has strong influence on T stability**

- **Structure of imidazolium CATION appears to have less influence, but more work is needed**

- **Influence of IMPURITIES on T stability of ionic liquids is not completely understood and is case-dependent.**

- **Intermediate chloride salts in synthetic route must be avoided due to residues in final ionic fluid (corrosion)**

- ***One-Step Synthesis** of ionic liquid mixtures:*

    a) **no chloride residues**

    b) **lower 'complexity' of synthetic process for ionic fluids**

    c) **possibly lower production cost**

    d) **synthetic methods must be optimized**

- **Can alternative ionic liquids be developed other than the imidazolium salts ?**